

Claims:

1. A method of forming a polycrystalline semiconductor film on a supporting substrate of foreign material, the method comprising:
 - i. Depositing a metal film onto a target surface of the substrate on which the polycrystalline semiconductor film is to be formed;
 - ii. Forming a film of metal oxide and/or metal hydroxide on a surface of the metal;
 - iii. Forming a layer of an amorphous semiconductor material over a surface of the metal oxide and/or metal hydroxide film;
 - iv. Heating the substrate, the metal, the metal oxide and/or metal hydroxide film and the amorphous semiconductor material to a temperature at which the semiconductor layer is absorbed into the metal layer and deposited onto the target surface by metal-induced crystallisation (MIC) as a polycrystalline layer, whereby the metal is left as an overlayer covering the deposited polycrystalline layer, with semiconductor inclusions in the metal layer, and the polycrystalline semiconductor film and the overlayer separated by a porous interfacial metal oxide and/or metal hydroxide film, with which the semiconductor inclusions are in contact;
 - v. Removing the metal in the overlayer and the interfacial metal oxide and/or metal hydroxide film with an etch which underetches the semiconductor inclusions to form freestanding islands weakly connected to the polycrystalline layer, without significantly thinning the underlying polycrystalline semiconductor layer;
 - vi. Removing the freestanding semiconductor "islands" from the surface of the polycrystalline semiconductor layer by a lift-off process.
2. The method of claim 1 wherein the substrate provides a planar base on which the semiconductor material is supported.
3. The method of claim 1 or 2 wherein a surface on which the semiconductor material is supported is textured to assist light trapping in the semiconductor material.
4. The method of claim 1, 2 or 3 wherein the substrate comprises a sheet of substrate material over which a preliminary layer is deposited and the target surface is a surface of the preliminary layer.
5. The method of claim 4 wherein which the preliminary layer is a silicon nitride or aluminium oxide or silicon oxide film.

6. The method as claimed in any one of claims 1 to 5 wherein, as a result of the MIC step, metal atoms are left in the polycrystalline layer which act as dopants and after the lift-off process, the polycrystalline semiconductor layer is doped with a dopant which overcompensates the doping caused by the metal atoms left in the polycrystalline layer after the MIC step, thereby causing the polycrystalline semiconductor layer to have an overall doping polarity which is opposite to that which would occur due to the metal atoms alone.
7. The method of claim 6 wherein the dopant overcompensation is achieved by depositing a spin-on dopant film onto the polycrystalline semiconductor film, heating of the sample, and removal of the spin-on dopant film.
8. The method of claim 6 wherein the dopant overcompensation is achieved by heating of the polycrystalline semiconductor layer in a gas atmosphere containing dopant atoms.
9. The method as claimed in any one of claims 1 to 5 wherein, as a result of the MIC step, metal atoms are left in the polycrystalline layer which act as dopants and the amorphous semiconductor material is doped during its formation with atoms that produce an opposite-polarity doping when compared to the polarity of doping caused by the metal atoms left in the polycrystalline layer after the MIC step, the opposite polarity doping being sufficient to overcompensate for the presence of the metal atoms whereby after the MIC step the net doping is opposite in polarity to that which would be produced by the metal atoms alone.
10. The method as claimed in any one of claims 1 to 9, wherein the substrate is a material selected from the group comprising sapphire, quartz, glass (including float glass, borosilicate glass and other glass types), metal, graphite, ceramics, plastics and polymers.
11. The method as claimed in any one of claims 1 to 10, wherein the polycrystalline semiconductor film is of a semiconductor material selected from the group comprising silicon, germanium, and an alloy of silicon and germanium.
12. The method as claimed in any one of claims 1 to 11 wherein the metal is selected such that the metal forms a eutectic solution with the selected semiconductor.
13. The method of claim 12 wherein the metal is selected from the group of metals comprising Be, Al, Zn, Ga, Ag, Cd, In, Sn, Sb and Au.
14. The method of claim 13 wherein the semiconductor is silicon and the metal is aluminium.

15. The method of claim 14 wherein an aluminium hydroxide film is formed by exposing the aluminium layer to an air atmosphere containing 100% relative humidity at room temperature ($22^{\circ} \pm 1^{\circ}$) for more than 1 hour at 1 atmosphere pressure.
16. The method of claim 14 wherein an aluminium hydroxide film is formed by
5 exposing the aluminium layer to an air atmosphere containing 100% relative humidity at room temperature ($22^{\circ} \pm 1^{\circ}$) for at least 24 hours at 1 atmosphere pressure.
17. The method of claim 14 wherein an aluminium oxide film is formed by exposing the aluminium layer to a dry air atmosphere (i.e. containing 0% relative humidity) at room temperature ($22^{\circ} \pm 1^{\circ}$) for more than 6 hours at 1 atmosphere
10 pressure.
18. The method of claim 14 wherein an aluminium hydroxide film is formed by exposing the aluminium layer to a dry air atmosphere (i.e. containing 0% relative humidity) at room temperature ($22^{\circ} \pm 1^{\circ}$) for at least 24 hours at 1 atmosphere pressure.
19. The method of claim 14 wherein a film comprising a mixture of aluminium
15 hydroxide and aluminium oxide is formed by exposing the aluminium layer to a semi-dry air atmosphere containing a relative humidity of more than 0% and less than 100% at room temperature ($22^{\circ} \pm 1^{\circ}$) for more than 1 hour at 1 atmosphere pressure.
20. The method of claim 14 wherein a film comprising a mixture of aluminium hydroxide and aluminium oxide is formed by exposing the aluminium layer to a semi-
20 dry air atmosphere containing a relative humidity of more than 0% and less than 100% at room temperature ($22^{\circ} \pm 1^{\circ}$) for at least 24 hours at 1 atmosphere pressure.
21. The method as claimed in any one of claims 1 to 20 wherein the metal and metal oxide and/or metal hydroxide etch is performed with a phosphoric acid solution.
22. The method of claim 21 wherein the phosphoric acid solution is a 100% solution
25 of 85% phosphoric acid, and the etch is performed at $130^{\circ}\text{C} \pm 3^{\circ}\text{C}$ for 20 minutes \pm 30 seconds.
23. The method as claimed in any one of claims 1 to 22 wherein the lift-off process is selected from the group comprising an acoustic treatment in a solution bath, a brush scrubbing process, or a hydrodynamic jet process.
- 30 24. The method as claimed in any one of claims 1 to 23 wherein the lift-off process is an brush scrubbing process.
25. The method as claimed in any one of claims 1 to 24 wherein the method further includes the step of, upon completion of the lift-off process, performing a uniform surface treatment to improve the surface finish of the sample prior to subsequent use of
35 the semiconductor film.

26. The method of claim 25 wherein the further step is an etch step comprising one or more etches selected from the group comprising a KOH etch, an NaOH etch, a HF/HNO₃ etch, a H₃PO₄ etch and an argon plasma etch.

27. The method as claimed in any one of claims 1 to 26 wherein the metal layer has
5 a thickness in the range of 30 – 500 nm.

28. The method as claimed in any one of claims 1 to 27 wherein the amorphous semiconductor layer used in the metal-induced crystallisation process has a thickness in the range of 30 – 750 nm.

29. The method of claim 28 wherein the metal layer has a thickness of 200 nm \pm 10
10 % and the amorphous semiconductor layer has a thickness of 300 nm \pm 10 %.

30. The method as claimed in any one of claims 1 to 29 wherein the metal-induced crystallisation is performed by annealing the sample at a temperature of 650 °C or less.

31. The method of claim 30 wherein the metal-induced crystallisation is performed by annealing the sample at a temperature of 500 °C or less for 2 hours.

15 32. The method as claimed in any one of claims 1 to 31, wherein the polycrystalline layer formed by metal-induced crystallisation on a foreign substrate is used as a seed layer for the formation of a further polycrystalline layer, the method further comprising:

Cleaning the surface of the seed layer to remove any oxides or other
20 contaminants;

Forming a second amorphous layer of a semiconductor material over the cleaned surface of the seed layer;

Heating the substrate, the seed layer and the second amorphous layer to crystallise the semiconductor material by solid phase epitaxy (SPE).

25 33. The method as claimed in claim 32 wherein the semiconductor material of the seed layer and the second amorphous layer are of the same semiconductor material with the same or different doping.

34. The method as claimed in claim 32 wherein the semiconductor material of the seed layer and the second amorphous layer are different semiconductor materials.

30 35. The method as claimed in claim 32 or 34 wherein the semiconductor material of the second amorphous layer is germanium or an alloy of silicon and germanium.

36. The method of claim 35 wherein the substrate, the seed layer and the second amorphous layer are heated to a temperature in the range of 200 – 650 °C to crystallise the semiconductor material by SPE.

35 37. The method as claimed in claim 32 or 33 wherein the second amorphous layer is silicon.

38. The method of claim 37 wherein the substrate, the seed layer and the second amorphous layer are heated to a temperature in the range of 520 – 560 °C for a period in the range of 15 to 20 hours to crystallise the semiconductor material.

39. The method of claim 38 wherein the substrate, the seed layer and the second
5 amorphous layer are heated to a temperature of $540 \pm 5^\circ\text{C}$ for a period of 17 ± 0.1 hours to crystallise the semiconductor material.

40. The method as claimed in any one of claims 32 to 39 wherein the second amorphous layer is simultaneously doped as it is formed.

41. The method of claim 37, 38 or 39 wherein the second amorphous layer is
10 simultaneously and progressively doped with gallium and then phosphorus as it is formed.

42. The method of claim 37, 38 or 39 wherein the second amorphous layer is simultaneously and progressively doped with boron and then phosphorus as it is formed.

15 43. The method as claimed in any one of claims 32 to 42 wherein the second amorphous semiconductor layer is formed by plasma enhanced chemical vapour deposition, sputtering, chemical vapour deposition, resistively heated evaporation or electron beam evaporation.

44. The method as claimed in any one of claims 32 to 42 wherein the second
20 amorphous semiconductor layer is formed in a vacuum electron beam evaporation process at a temperature of 20 - 400 °C.

45. The method of claim 44 wherein the second amorphous semiconductor layer is formed in a vacuum electron beam evaporation process at a temperature of $150^\circ\text{C} \pm 20^\circ\text{C}$ and at a pressure of less than 5×10^{-7} Torr.

25 46. The method of claim 45 wherein the semiconductor deposition process to deposit the second amorphous semiconductor layer is performed at a pressure of less than 1×10^{-7} Torr.

47. The method of claims 44, 45 or 46 wherein the second amorphous semiconductor layer is formed in a electron beam evaporation process with a deposition
30 rate of up to 2 $\mu\text{m}/\text{min}$.

48. The method as claimed in any one of claims 44 to 47 wherein the second amorphous semiconductor layer is deposited at a rate of 100 nm/min or more.

49. The method of claim 48 wherein the second amorphous semiconductor layer is formed in an electron beam evaporation process with a deposition rate of 250 ± 20
35 nm/min.

50. The method as claimed in any one of claims 32 to 49 wherein the amorphous semiconductor material of the second amorphous semiconductor layer is doped to a predetermined doping profile during an electron beam evaporation deposition process using resistively heated p-type and n-type dopant effusion cells in the vacuum electron-
5 beam evaporation chamber while the deposition process takes place.
51. The method as claimed in any one of claims 32 to 50 wherein the substrate, the seed layer and the second amorphous semiconductor layer are heated in a vacuum furnace.
52. The method as claimed in any one of claims 32 to 50 wherein the substrate, the
10 seed layer and the second amorphous semiconductor layer are heated in an atmospheric furnace.
53. The method as claimed in any one of claims 32 to 52 wherein the substrate, the seed layer and the second amorphous semiconductor layer are heated by radiative heating.
- 15 54. The method as claimed in any one of claims 37 to 39, 41, or 42 wherein the step of cleaning the seed layer surface comprises a process which creates a hydrogen-terminated silicon surface and the substrate is transferred to the semiconductor deposition chamber within 60 minutes of completion of the cleaning step.
55. The method of claim 54 wherein the step of cleaning the seed layer surface
20 comprises the further steps of:
- i. immersing the surface for 10 minutes in a fresh 1:1 mixture of hydrogen peroxide and sulfuric acid ;
 - ii. rinsing the surface in de-ionized water;
 - iii. immersing the surface for 30 seconds in diluted (5%) hydrofluoric
25 acid;
 - iv. immersing the surface in de-ionized water; and
 - v. drying the surface with gaseous nitrogen.
56. The method as claimed in any one of claims 37 to 39, 41, 42, 54 or 55 wherein after the step of crystallisation by solid phase epitaxy, a further high-temperature anneal
30 is performed at a temperature in the range 700 - 1000 °C for a period of less than five minutes to increase the fraction of electrically active dopant atoms in the crystalline semiconductor material.
57. A method of forming a film of polycrystalline semiconductor material on a supporting substrate of foreign material, the method comprising:

- i. Forming a polycrystalline seed layer of a seed layer semiconductor material onto a target surface of the substrate on which the polycrystalline semiconductor film is to be formed.
 - ii. Cleaning the surface of the seed layer to remove any oxides or other contaminants;
 - iii. Forming over the cleaned surface of the seed layer an amorphous layer of the semiconductor material to become the polycrystalline film;
 - iv. Heating the substrate, the seed layer and the amorphous layer to crystallise the amorphous semiconductor material by solid phase epitaxy (SPE).
58. The method of claim 57 wherein the substrate provides a planar base on which the semiconductor material is supported.
59. The method of claim 57 or 58 wherein a surface on which the semiconductor material is supported is textured to assist light trapping in the semiconductor material.
60. The method of claims 57, 58 or 59 wherein the step of forming the amorphous layer of semiconductor material over the cleaned surface of the seed layer comprises forming an amorphous semiconductor layer by evaporation.
61. The method of claim 60 wherein the step of forming the amorphous layer of semiconductor material over the cleaned surface of the seed layer comprises placing the substrate in a high-vacuum electron-beam evaporation chamber with a source of the semiconductor material and forming an amorphous layer of the semiconductor material over the cleaned surface of the seed layer using a high-vacuum, electron-beam evaporation deposition process;
62. The method of claims 57, 58 or 59 wherein the step of forming the amorphous layer of semiconductor material over the cleaned surface of the seed layer comprises forming an amorphous semiconductor layer by plasma enhanced chemical vapour deposition.
63. The method of claims 57, 58 or 59 wherein the step of forming the amorphous layer of semiconductor material over the cleaned surface of the seed layer comprises forming an amorphous semiconductor layer by sputtering.
64. The method of claims 57, 58 or 59 wherein the step of forming the amorphous layer of semiconductor material over the cleaned surface of the seed layer comprises forming an amorphous semiconductor layer by chemical vapour deposition,
65. The method as claimed in any one of claims 57 to 64 wherein the substrate comprises a sheet of substrate material over which a preliminary layer is deposited and the target surface is a surface of the preliminary layer.

66. The method of claim 65 wherein which the preliminary layer is a silicon nitride or aluminium oxide or silicon oxide film.
67. The method as claimed in any one of claims 57 to 66, wherein the second amorphous layer is silicon.
- 5 68. The method as claimed in claim 67 wherein the substrate, the seed layer and the amorphous semiconductor layer are heated to a temperature in the range of 520 – 560 °C for a period in the range of 15 to 20 hours to crystallise the amorphous semiconductor material.
69. The method of claim 68 wherein the sample is heated to a temperature of $540 \pm$
10 5°C for a period of 17 ± 0.1 hours to crystallise the amorphous semiconductor material.
70. The method as claimed in any one of claims 57 to 65 wherein the semiconductor material of the second amorphous layer is germanium or an alloy of silicon and germanium.
- 15 71. The method of claim 70 wherein the substrate, the seed layer and the second amorphous layer are heated to a temperature in the range of 200 – 650 °C to crystallise the semiconductor material by SPE.
72. The method as claimed in any one of claims 67 to 69 wherein the amorphous silicon layer is formed at a temperature of 20 - 400 °C.
- 20 73. The method as claimed in any one of claims 57 to 72 wherein the semiconductor material of the seed layer and the SPE polycrystalline layer are the same semiconductor material with the same or different doping.
74. The method as claimed in any one of claims 57 to 72 wherein the semiconductor material of the seed layer and the SPE polycrystalline layer are different semiconductor
25 materials.
75. The method as claimed in any one of claims 57 to 74 wherein the amorphous layer is simultaneously doped as it is formed.
76. The method of claim 67, 68, 69 or 72 wherein the amorphous layer is simultaneously and progressively doped with gallium and then phosphorus as it is
30 formed.
77. The method of claim 67, 68, 69 or 72 wherein the amorphous layer is simultaneously and progressively doped with boron and then phosphorus as it is formed.
78. The method of claim 72, 76 or 77 wherein the amorphous layer is formed at a
35 temperature of $150^\circ\text{C} \pm 20^\circ\text{C}$ and at a pressure of less than 5×10^{-7} Torr.

79. The method of claim 78 wherein the semiconductor deposition process to deposit the amorphous layer is performed at a pressure of less than 1×10^{-7} Torr.

80. The method as claimed in any one of claims 57 to 79 wherein the amorphous layer is formed in an electron beam evaporation process with a deposition rate of up to
5 2 $\mu\text{m}/\text{min}$.

81. The method of claim 80 wherein the amorphous layer is deposited at a rate of 100 nm/min or more.

82. The method of claim 80 or 81 wherein the amorphous layer is formed with a deposition rate of 250 ± 20 nm/min.

10 83. The method as claimed in any one of claims 57 to 85 wherein the semiconductor material of the amorphous layer is doped to a predetermined doping profile during the deposition process using resistively heated p-type and n-type dopant effusion cells in the vacuum electron-beam evaporation chamber while the deposition process takes place.

15 84. The method as claimed in any one of claims 57 to 83 wherein the substrate, the seed layer and the amorphous semiconductor layer are heated in a vacuum.

85. The method as claimed in any one of claims 57 to 83 wherein the substrate, the seed layer and the amorphous semiconductor layer are heated in an atmospheric furnace.

20 86. The method as claimed in any one of claims 57 to 85 wherein the substrate, the seed layer and the amorphous semiconductor layer are heated by radiative heating.

87. The method as claimed in any one of claims 67, 68, 69, 72, 76, 77, 78, or 79 wherein the semiconductor material is silicon and the cleaning step comprises a process which creates a hydrogen-terminated silicon surface and the substrate is transferred to
25 the semiconductor deposition chamber within 60 minutes of completion of the cleaning step.

88. The method of claim 87 wherein the step of cleaning the seed layer surface comprises the further steps of: -

- 30 vi. immersing the surface for 10 minutes in a fresh 1:1 mixture of hydrogen peroxide and sulfuric acid;
- vii. rinsing the surface in de-ionized water;
- viii. immersing the surface for 30 seconds in diluted (5%) hydrofluoric acid;
- ix. immersing the surface in de-ionized water; and
- 35 x. drying the surface with gaseous nitrogen.

89. The method as claimed in any one of claims 57 to 88 wherein the substrate is a material selected from the group comprising quartz, glass (including float glass, borosilicate glass and other glass types), metal, graphite, ceramics, plastics and polymers.

- 5 90. The method as claimed in any one of claims 67, 68, 69, 72, 76, 77, 78, 79 or 88 wherein after the step of crystallisation by solid phase epitaxy, a further high-temperature anneal is performed at a temperature in the range 700 - 1000 °C for a period of less than five minutes to increase the fraction of electrically active dopant atoms in the crystalline semiconductor material.